Bis(*ortho*)-Chelated Bis(phosphanyl)aryl Ruthenium(II) Complexes Containing an η^1-*P*-Monodentate or μ-Bridging η^1-*P*,η^1-*P*′ Bonded R−PCHP Arene Ligand, 1-R-3,5-$(CH_2PPh_2)_2C_6H_3$ [R = H, Br, or, Si(*n*-$CH_2CH_2C_8F_{17})_3$] — Cyclometalation Reaction Intermediates and Potential Catalysts for Use in Fluorinated Biphasic Systems

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Mono- and binuclear ruthenium(II) complexes containing ligands derived from the *meta*-bis(phosphanyl)arene ligand 1-R-3,5-$(CH_2PPh_2)_2C_6H_3$ [R–PCHP: R = H (**5**), Br (**3**), or Si(*n*-$CH_2CH_2C_8F_{17})_3$ (**4**)] have been synthesized and fully characterized. On reaction of equimolar amounts of the ruthenium starting material (e.g. $[RuCl_2(PPh_3)_3]$) and the *meta*-bis(phosphanyl)arene, complexes of the type $[RuCl\{C_6H_2(CH_2PPh_2)_2$-2,6-R-4$\}(PPh_3)]$ are invariably isolated, which contain only one $[C_6H_3(CH_2PPh_2)_2$-2,6$]^-$ monoanionic ligand η^3-*P,C,P*′-bonded to Ru. Monitoring of this reaction by ^1H and ^{31}P NMR has shown it to proceed via intermediate species having an apparently η^3-*P,C,P*′-bonded PCP ligand and a second *meta*-bis(phosphanyl)arene ligand that is either η^1-P-bonded or μ-η^1-P,η^1-P′-bridging between two [RuCl(PCP)] units. The synthesis of the first PCP "pincer"-type ligand with a polyfluorinated "pony tail" is detailed, viz. compound **4** as well as the corresponding ruthenium complex [RuCl{(*n*-C_8F_{17}-$CH_2CH_2)_3$Si–PCP}], **7**. The latter compound is soluble in fluorinated solvents and hence represents the first ruthenium "pincer" complex that may find use in fluorinated biphasic systems.

Introduction

Bis(phosphanes) exhibit a rich coordination chemistry upon interaction with a wide range of metal centers. As shown in Figure 1, various mono- and multimetallic complexes can be formed. Complexes with *cis*-η^2-*P,P*′-coordinated ligands are by far the most common as compared with the so-called "dangling" η^1-*P* (monodentate) coordination motif.[1] The coordination mode can be greatly affected by the length of the chain linking the two donor groups and by the type of substituents present either in the organic backbone or at the donor atoms.[2] The use of bis(phosphane) ligands capable of forming *trans*-spanning complexes (often with a carbon chain containing five or more atoms) is likely to lead to the observation of a different binding mode. This involves not only the coordination of the two P-donors, but also that of a formal carbanion localized at a central position in the backbone. This is clearly a result of C−H bond activation (i.e. orthometalation).[3] Thus, true organometallic species can be generated from bis(phosphane) ligands through appropriate choice of the linking backbone. This is exemplified by the "pincer" ligands of the general formula shown in Figure 1 (the monoanionic η^3-*P,C,P*′-coordinating PCP ligand) and Figure 2.

Such properties of *trans*-spanning ligands are particularly evident in the coordination behavior of bis(phosphane) ligands of the type R−PCHP (Figure 2), in which a rigid *m*-xylylenediyl organic fragment links the two P donor groups.[3a,4]

Reaction of these R−PCHP ligands with transition metal complexes frequently results in the formation of metalated complexes containing a formal monoanionic (i.e. η^3-*P,C,P*′)-coordinated R−PCP ligand. Only a few cases are known where the ligand is bonded as a neutral (noncyclometalated) R−PCHP species. Examples of this type of bonding are observed in just a few square-planar d^8 metal complexes,[5−7] tetrahedral silver compounds,[8] and the octahedral ruthenium species **1**[9] and **2**[10] (Figure 3).

In the present paper, the coordination and cyclometalation properties of the R−PCHP ligands 1-Br-3,5-$(CH_2PPh_2)_2C_6H_3$ (**3**), 1-(*n*-$C_8F_{17}CH_2CH_2)_3$Si-3,5-$(CH_2PPh_2)_2C_6H_3$ (**4**), and 3,5-$(CH_2PPh_2)_2C_6H_4$ (**5**) (R = H, see Figure 2) are reported in more detail. The formation of species with *P*-coordinated neutral R−PCHP ligands and their involvement in the generation of cyclometalated compounds with monoanionic η^3-*P,C,P*′-coordinated R−PCP ligands has been observed.

Results and Discussion

Ruthenium Complexes of R−PCP Ligands

The fluorine-rich ligand (*n*-$C_8F_{17}CH_2CH_2)_3$Si−PCHP (**4**) (Scheme 1) was obtained in excellent yield (94%) by dir-

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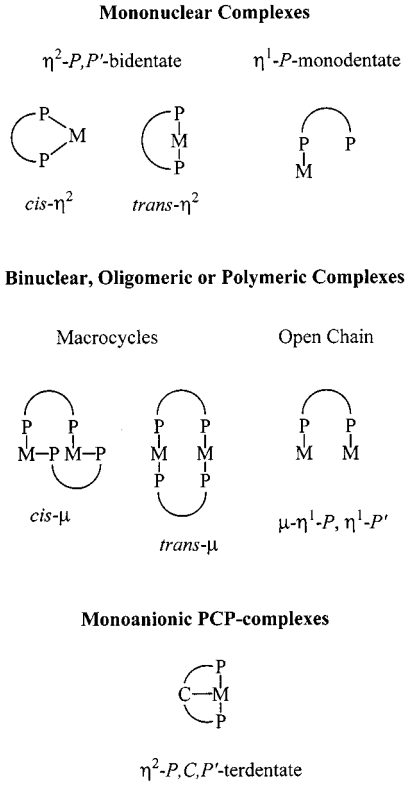


Figure 1. Possible coordination modes of bis(phosphane) ligands and of a monoanionic η^3-*P,C,P′*-coordinated PCP ligand derived from C−H activation

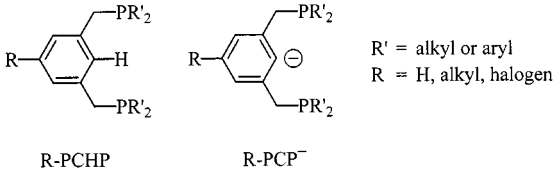


Figure 2. R−PCHP-type ligands and their respective monoanionic R−PCP derivatives

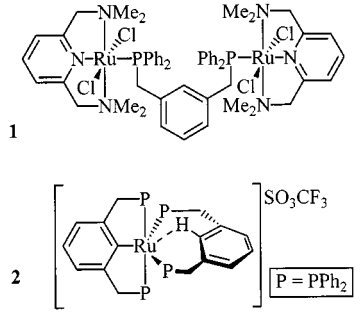
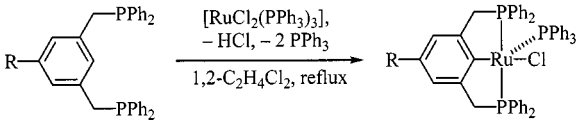


Figure 3. Octahedral ruthenium species with a neutral PCHP ligand

ect lithium/halogen exchange of the 5-bromo *meta*-bis(phosphane) ligand **3** with two equiv. of *t*BuLi followed by quenching of the resulting 5-lithio derivative with $(n\text{-}CH_2CH_2C_8F_{17})_3SiBr$. Reactions of **3** and **4** with one equiv. of $[RuCl_2(PPh_3)_3]$ in refluxing 1,2-dichloroethane (Scheme 1) resulted in the formation of the 16-electron, neutral ruthenium(II) compounds [RuCl{$C_6H_2(CH_2PPh_2)_2$-2,6-R-4}(PPh_3)] [R = Br, **6**; $(n\text{-}C_8F_{17}CH_2CH_2)_3Si$, **7**], containing a monoanionic η^3-*P,C,P′*-bonded R−PCP ligand, in about 70% yield in each case.



3, R = Br
4, R = Si(n-$CH_2CH_2C_8F_{17}$)$_3$
5, R = H

6 (72%)
7 (71%)
8 (90%)[12-14]

Scheme 1. Synthesis of [RuCl(R−PCP)(PPh_3)] complexes

In the $^{31}P\{^1H\}$ NMR spectrum of **6**, the phosphorus resonance attributable to the cyclometalated Br−PCP ligand appears as a doublet at $\delta = 36.74$ while the phosphorus nucleus of the PPh_3 moiety resonates as a triplet at $\delta = 80.62$ ($^2J_{PP} = 32$ Hz). A coupling constant of this magnitude is characteristic of a *cis* arrangement of the PPh_3 unit in relation to the two magnetically equivalent PCP phosphorus nuclei.[11] The ^1H NMR spectrum of **6** shows a set of two multiplets attributable to the diastereotopic benzylic protons, indicating the absence of a plane of symmetry containing the benzylic carbon atoms, but showing the presence of an apparent plane of symmetry bisecting the Ru−Cl−P(PPh_3)−C_{ipso} atoms. This leads to enantiotopic *ortho*-CH_2PPh_2 substituents. Similar ^1H and ^{31}P NMR spectra have been observed for the fluorinated-tail complex **7**. In addition to the respective resonances observed for **6**, the ^1H NMR spectrum of **7** shows two multiplets in the ranges $\delta = 0.90-1.10$ and $1.95-2.25$, each set of signals integrating for six protons, clearly attributable to the methylene protons present in the fluorinated chain.

All the spectroscopic features suggest that **6** and **7** are structural analogues of the reported parent complex [RuCl(H−PCP)(PPh_3)] (**8**, cf. **6** with R = H).[12−14] Thus, these new complexes have a distorted square-pyramidal geometry in solution, with a PPh_3 ligand in the apical position and a basal plane formed by the monoanionic η^3-*P,C,P′*-coordinated R−PCP ligand and the Cl ligand.

Ruthenium Complexes Containing One Neutral R−PCHP Ligand

The method outlined in Scheme 1 was one of our initial synthetic protocols that we applied to the synthesis of [RuCl(R−PCP)(PPh_3)] [R = H (**8**), Ph][12] complexes. This method has proven to be of general use. However, some drawbacks have been encountered for R groups containing sensitive functionalities (e.g., when R = $SiMe_3$, desilylation can occur).[10,15] Other chlorinated solvents can be used as the reaction medium, such as CH_2Cl_2 or *o*-dichlorobenzene. However, 1,2-dichloroethane has been shown to be the best choice in terms of reaction times (typically 1−2 h), yields, and ease of work-up of the resulting products. When the reactions are carried out in refluxing CH_2Cl_2, the lower temperature leads to an appreciable decrease in the rate of the reaction such that the final complex is obtained only after three days. On the other hand, this retardation has allowed us the opportunity to gain insight into the various

stages of the reaction leading to the formation of species such as **6** and **8**.

On monitoring the 1:1 molar reaction of **3** with $[RuCl_2(PPh_3)_3]$ in refluxing CH_2Cl_2 by ^{31}P NMR spectroscopy, the signal attributable to **3** ($\delta = -9.07$) is seen to disappear within 5 min. At the same time, a broad and intense singlet at $\delta \approx -4.5$ is observed, which is characteristic of free PPh_3, together with intense but very broad signals between $\delta = 30$ and 90. This suggests the occurrence of intra- and/or intermolecular exchange processes involving displacement of PPh_3 ligand(s) of $[RuCl_2(PPh_3)_3]$ by the more basic benzylic ligand **3**. This results in the formation of a complex mixture of oligomeric species. Within 1−2 h, the broad signals gradually fade in intensity with the concomitant appearance of a set of two doublets located at $\delta =$ 40.05 and 40.30 (the latter is normally very weak), a triplet at $\delta = 83.75$ ($J_{PP} = 30$ Hz), and a singlet at $\delta = -10.06$. At this stage, it is already possible to observe very weak patterns due to the final compound **6** (doublet and triplet resonances at $\delta = 36.74$ and 80.62, respectively). Obviously, as the reaction progresses the signals due to **6** become stronger at the expense of the other signals present. It should be noted that similar behavior was observed when ligand **5** was used in such an experiment.

The magnitude and multiplicity of J_{PP} gives an excellent indication of the mutual arrangement of the phosphanes[11] around the metal center and allows the assignment of structural features of the intermediate species formed en route to the final product (e.g. **6**). The coupling constant data pointed to the presence of Ru complexes containing an η^2-*P,P′*-bonded ligand as exemplified, for instance, by structures **A** and **B** (Figure 4). Such complexes have often been postulated as precursors in cyclometalations of bis(phosphane) donor ligands. However, the chemical shifts are typical for a bis(*ortho*)-metalated η^3-*P,C,P′*-bonded PCP ligand containing a third phosphorus nucleus in an apical position *trans* to a vacant site.[10−13,16] For instance, in the ^{31}P NMR spectrum of the cationic Ru^{II} complex **2**, the only known complex containing both an η^2-*P,P′* PCHP and an η^3-*P,C,P′*-coordinated PCP ligand attached to the same metal center, the ^{31}P resonance of the P nuclei of the bidentate bonded *meta*-bis(phosphane) PCHP ligand is seen at around $\delta = 18-20$, while the nuclei of the η^3-*P,C,P′*-coordinated PCP ligand give rise to a broad signal (room temp.) centered at $\delta = 40$.[17] Therefore, the initially formed species consists of the μ-η^1-*P*,η^1-*P′* (cf. **C**) or the η^1-*P*-coordinated species **D** (Figure 4). The latter compounds already contain a bis(*ortho*)-metalated η^3-*P,C,P′* R−PCP ligand but differ from the final complex **6** in that the apical position is occupied by a second R−PCHP ligand instead of PPh_3. In this way, the singlet at $\delta = -10.06$ can be assigned to the dangling PPh_2 group of **D** and the doublet at $\delta = 40.30$ to the phosphorus of the bis(*ortho*)-metalated ligand. On this basis, the signal at $\delta = 83.75$ should therefore be comprised of two superimposed triplets.

In accordance with this hypothesis, compounds **9** and **10** were detected when $[RuCl_2(PPh_3)_3]$ was reacted with excess Br−PCHP (2 to 3 equiv. of Br−PCHP were used instead of 1, cf. step *a* in Scheme 2), and when **6** was directly reacted with one equiv. of Br−PCHP (step *b* in Scheme 2). Furthermore, the addition of further $[RuCl_2(PPh_3)_3]$ to a mixture of complexes **9** and **10** (CH_2Cl_2) followed by refluxing overnight (step *c* in Scheme 2) afforded **6** in 53% isolated yield.

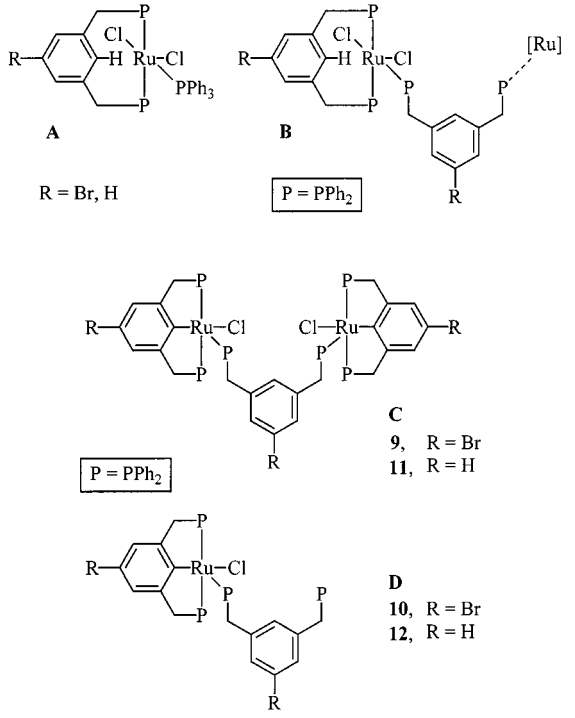
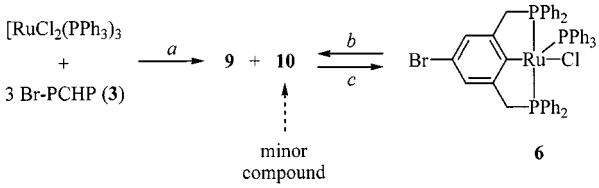


Figure 4. Postulated and observed intermediates in cyclometallation of bis(phosphane) donor ligands



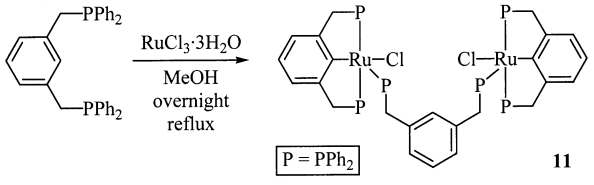
Scheme 2. Conditions: (a) CH_2Cl_2, reflux for 3 days; (b) 1 equiv. of Br−PCHP, CH_2Cl_2, 1 h at room temp.; (c) 1 equiv. of $[RuCl_2(PPh_3)_3]$, CH_2Cl_2, overnight reflux

From the ^1H and ^{13}C NMR spectra of a mixture of **9** and **10** (the latter present to an extent of 11%), most of the features of **9** and some of the features of **10** could be established. Thus, the presence of a bis(*ortho*)-metalated Br−PCP ligand is clearly apparent from the ^{13}C NMR spectrum, where $Ru-C_{ipso}$ of **9** appears at $\delta = 173.85$ as a characteristic doublet ($^2J_{CP} = 16$ Hz).[14] The diastereotopic benzylic protons of the cyclometalated ligand give rise to signals at $\delta = 2.67$ and 3.63 in the ^1H NMR spectrum, each with integrals corresponding to four protons. On the other hand, all of the benzylic protons of the bridging Br−PCHP ligand appear as a single doublet at $\delta = 3.10$ ($^2J_{HP} = 9$ Hz). The aromatic protons of the xylylene group of the Br−PCHP ligand give rise to two singlets at considerably higher field, at $\delta = 4.82$ and 5.47, respectively, with relative integrals of 1:2. These features further confirm the idealized square-pyramidal structure of this compound and emphas-

ize the symmetric disposition of the bridging ligand, where the diastereotopic benzylic protons are magnetically equivalent. In the case of **10**, two of the benzylic protons of the bis(*ortho*)-metalated ligand and all the benzylic protons of the η^1-*P*-bonded Br−PCHP ligand are coincidentally located in the same spectral region (δ = 3.30−3.80), while the two remaining benzylic protons appear as a multiplet at δ = 2.83. The xylylene protons of the Br−PCHP ligand are nonequivalent and appear as singlets at δ = 5.68, 5.82, and 5.90. It should be mentioned that transition metal complexes containing a neutral η^1-*P* monodentate R−PCHP ligand have not previously been reported. To the best of our knowledge, this coordination mode has only been observed in Ag compounds of the H−PCHP ligand (P = PPh_2).[25]

The **C**- and **D**-type species were also observed in similar reactions involving **5** (i.e. complexes **11** and **12**). However, in the case of the H−PCHP ligand, the concentration of species **12** was too low to allow its characterization by ^1H and ^{13}C NMR spectroscopy.

Further evidence for the absence of PPh_3 in complexes such as **C** was obtained from the reaction of $RuCl_3 \cdot 3H_2O$ with an excess of H−PCHP in methanol (Scheme 3). Spectroscopically pure complex **11** was isolated as a green solid in low yield (14%). Similar spectroscopic features to those of **9** were observed, with the exception of the multiplicity of the xylylene protons of the bridging H−PCHP ligand. In **11**, they appear as a singlet (δ = 5.42), a doublet (δ = 5.69, $^3J_{HH}$ = 8 Hz), and a triplet (δ = 5.99, $^3J_{HH}$ = 8 Hz).



Scheme 3. Formation of **11** using $RuCl_3 \cdot 3\,H_2O$ as starting material

The fluorinated arylruthenium(II) "pincer" complex **7** is the first example of a ruthenium compound containing three fluorinated C_{10} tails ("pony tails") connected to the *para*-position of the PCP ligand through a silicon branching point. A very interesting feature of **7**, which has 43.2 wt% of fluorine, is its solubility in fluorocarbon solvents. Initially, **7** was synthesized to facilitate the separation of the arylruthenium(II) compound from the free PPh_3 present in the crude reaction mixture. Thus, the mixture could be separated by dissolving **7** in FC-72 (perfluorohexanes), a solvent in which PPh_3 is insoluble. This property also gives a clear indication of the presence of an $(n\text{-}C_8F_{17}CH_2CH_2)_3Si$ group in the complex molecule for species such as **6** and **8**, which would otherwise be completely insoluble in FC-72. Our intention for **7** and analogous fluorinated organometallic compounds is to explore their chemistry in fluorinated biphasic catalysis.[18] In this context, we have already prepared the NCN complex **13** (Figure 5) containing 35.8 wt% of fluorine, and have used it as a model complex for the selective addition of CCl_4 to methyl methacrylate (Kharasch addition) under both standard and fluorinated biphasic conditions.[19,20]

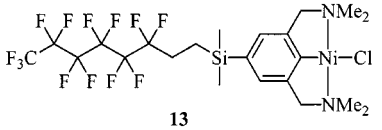


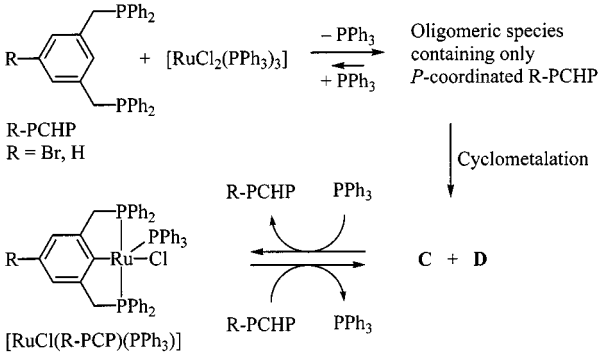
Figure 5. Fluorinated arylruthenium(II) pincer **13** used for the Kharasch addition reaction under biphasic conditions

It is interesting to note that in the syntheses of **6** and **7**, the Br−C and Si−C bonds remain unaffected by the applied synthetic protocol. This is in sharp contrast to the Si−aryl bond cleavage observed using the ligand Me_3Si−PCHP under similar conditions.[13,15] Such a process (i.e. desilylation) is thought to be promoted by HCl formed in the ruthenation reaction[13,15] and to follow an electrophilic aromatic substitution mechanism.[21] Therefore, the presence of electron-withdrawing groups on the aromatic ring can be expected to disfavor such reactivity. Indeed, it is observed that the electron density at the Si atom, as measured by ^{29}Si NMR spectroscopy, is significantly lower in $(n\text{-}C_8F_{17}CH_2CH_2)_3Si$−aryl compounds than in their Me_3Si−aryl analogues.[22]

Oxidative addition of low-valent (coordinatively unsaturated) ruthenium complexes to C−halide bonds is a well-documented process.[23] However, in the synthesis of **6** no species originating from this type of reactivity were detected and the retention of the C−Br bond in the product was clearly established by ^{13}C NMR spectroscopy and elemental analysis. This bond was also unaffected during an attempt to form a bimetallic complex through the coupling of two molecules of **6**. This was performed in combination with a nickel-containing catalyst. The starting complex **6** was recovered quantitatively at the end of the procedure.

The observations made thus far suggest that the displacement of the η^1-*P* or μ-η^1-*P*,η^1-*P*′ bonded R−PCHP ligand from species such as **C** and **D** is probably the rate-limiting step of this reaction, rather than the C−H activation that occurs during the cyclometalation step. In the early stages of the reaction of $[RuCl_2(PPh_3)_3]$ with R−PCHP, the latter readily displaces the PPh_3 ligands coordinated at the ruthenium center, forming a mixture of species, most likely oligomeric in nature (Scheme 4). The extent to which this process occurs is likely to be dictated by the chelate-coordinative properties of the R−PCHP ligand relative to those of PPh_3. A fast and, under the applied reaction conditions, irreversible cyclometalation reaction proceeds, this being the origin of species of types **C** and **D**. As in this reaction the molar ratio of $[RuCl_2(PPh_3)_3]$ to R−PCHP is 1:1, the formation of complexes such as **C** and **D** implies the existence of Ru centers depleted of such ligands. The excess free PPh_3 present slowly displaces coordinated R−PCHP ligands, which are then trapped by the metal centers lacking a cyclometalated R−PCP ligand. Therefore, one of the roles of complexes such as **9**, **10**, **11**, and **12** in the formation of [RuCl(R−PCP)(PPh_3)] complexes would appear to be to serve as reservoirs of R−PCHP ligands. Naturally, the R−PCHP released from species **C** and **D** can also react

with the final complex [RuCl(R−PCP)(PPh_3)], replacing the PPh_3 and reforming **C** and **D**. However, this does not lead to any progress in the overall process in the direction of formation of complexes [RuCl(R−PCP)(PPh_3)].



Scheme 4. Formation of [RuCl(R−PCP)(PPh_3)] complexes by reacting [$RuCl_2(PPh_3)_3$] with R−PCHP ligands

Conclusions

In this paper, we have focussed on the reaction of the [$RuCl_2(PPh_3)_3$] starting material with R−PCHP ligands having PPh_2 groups connected through a rigid *m*-xylylenediyl organic fragment. When equimolar amounts of [$RuCl_2(PPh_3)_3$] and the R−PCHP ligands were mixed, a chemo- and regioselective reaction was observed involving one of the C−H bonds of the *m*-xylylenediyl fragment, thereby leading to the exclusive formation of complexes of the type [RuCl(R−PCP)(PPh_3)]. Analysis carried out in the course of the reaction has shown the intermediacy of monomeric and dimeric Ru complexes containing an η^3-*P,C,P′* R−PCP ligand and an η^1-*P* R−PCHP ligand bonded to the same metal center. The displacement of the R−PCHP ligand apparently constitutes the rate-determining step in this reaction, and hence C−H bond activation does not greatly affect the overall rate. In this sense, the observed intermediates operate as reservoirs, slowly releasing R−PCHP fragments during the course of the reaction.

In the R−PCHP-type ligand, the R group, located in the *meta*-position in relation to the two CH_2PPh_2 fragments, offers an additional potentially reactive site to the metal center or to species present in the reaction mixture under the employed conditions. However, no interactions involving this part of the ligand molecule were observed.

Finally, complex **7** represents the first example of an Ru compound bearing three fluorinated tails connected to the *para*-position of a PCP ligand. An interesting solubility in a fluorinated solvent (FC-72) has been shown, which is a prerequisite for future investigations concerning the use of **7** as a catalyst or catalyst precursor in biphasic systems.

Experimental Section

General Remarks: All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Benzene, alkanes, and Et_2O were dried with sodium using benzophenone as indicator. Dichloromethane was dried with CaH_2. 1,2-Dichloroethane and FC-72 were degassed using the freeze-pump-thaw technique. − ^1H, ^{13}C, ^{19}Si, and ^{31}P NMR spectra were recorded at 25 °C on a Bruker AC200 or on a Varian Unity INOVA 300 NMR spectrometer. Chemical shifts are given in ppm relative to $(CH_3)_4Si$ (^1H, ^{13}C, and ^{19}Si NMR spectra) or a capillary containing 85% H_3PO_4 (^{31}P NMR spectra). − 5-Bromo-*m*-xylene was purchased from Aldrich Chem. Co. and was used without further purification. [$RuCl_2(PPh_3)_3$],[24] **5**,[25] **8**,[12] 1-Br-3,5-$(CH_2Br)_2C_6H_3$,[26] and $BrSi(n\text{-}CH_2CH_2C_8F_{17})_3$ [27] were prepared according to literature procedures. Attempted homocouplings using a nickel catalyst were performed following a procedure described previously.[28]

Synthesis of 1-Br-3,5-$(CH_2PPh_2)_2C_6H_3$ (3): A three-necked 500 mL round-bottomed flask containing an ammonia condenser and a magnetic stirring bar was connected to a nitrogen line and then immersed in an acetone/dry-ice bath. After about 250 mL of ammonia had been condensed, sodium (1.38 g, 60 mmol) was added in small chunks. After 30 min, solid PPh_3 (7.87 g, 30 mmol) was added to the intensely blue-colored solution, causing a color change to pale-yellow. After a further 40 min, dry ammonium bromide (2.94 g, 30 mmol) was slowly added, followed after another 15 min by solid 1-Br-3,5-$(CH_2Br)_2C_6H_3$ (5.14 g, 15 mmol) in a single portion. The acetone/dry-ice bath was then removed. After evaporation of the ammonia (4 h), the residual material was extracted with degassed water (2 × 100 mL) and diethyl ether (4 × 100 mL). The combined organic extracts were dried with $MgSO_4$. After filtration, the volatiles were removed in vacuo from the filtrate to leave a white solid. Recrystallization from MeOH was sometimes necessary to purify the compound. Yield: 60−70%. − $C_{32}H_{27}BrP_2$ (553.5): calcd. C 69.45, H 4.92; found C 69.41, H 4.88. − M.p. 95−97 °C. − ^1H NMR (200 MHz, $CDCl_3$): δ = 3.26 (s, 4 H, CH_2), 6.75 (s, 1 H, CH-4), 6.91 (s, 2 H, CH-2,6), 7.20−7.45 (m, 20 H, aromatic). − $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 35.9 (d, $^1J_{CP}$ = 17 Hz, CH_2), 122.2 (s, CBr), 128.7 (d, $^3J_{CP}$ = 7 Hz, *m*-Ph), 129.1 (s, *p*-Ph), 129.4 (t, $^3J_{CP}$ = 7 Hz, CH-4), 130.1 (d, $^3J_{CP}$ = 9 Hz, CH-2,6), 133.1 (d, $^2J_{CP}$ = 19 Hz, *o*-Ph), 138.1 (d, $^1J_{CP}$ = 15 Hz, C_{quat} of Ph), 139.8 (d, $^2J_{CP}$ = 9 Hz, C-3,5). − $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ = −9.07 (s).

Synthesis of 1-Si(n-$CH_2CH_2C_8F_{17})_3$-3,5-$(CH_2PPh_2)_2C_6H_3$ (4): To a solution of **3** (1.11 g, 2 mmol) in diethyl ether (50 mL) at −80 °C was added 2 equiv. of a hexane solution of *t*BuLi. After 40 min., a solution of $BrSi(n\text{-}CH_2CH_2C_8F_{17})_3$ (2.90 g, 2 mmol) in diethyl ether (80 mL) was transferred into the organolithium solution at −80 °C by means of a cannula. After 1 h, the system was slowly allowed to warm to room temperature (overnight). A $^{31}P\{^1H\}$ NMR spectrum recorded thereafter indicated quantitative conversion. Compound **4** was separated from the LiBr by repeated extractions with pentane. Yield: 3.46 g (1.9 mmol, 94%). − $C_{62}H_{39}F_{51}P_2Si$ (1842.9): calcd. C 40.41, H 2.13, F 52.58, P 3.36, Si 1.52; found C 40.54, H 2.23, F 52.46, P 3.28, Si 1.55. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85−0.97 (m, 6 H, CH_2−Si), 1.80−2.10 (m, 6 H, CH_2−CF_2), 3.45 (s, 4 H, CH_2−P), 6.65 (m, 2 H, CH-2,6), 7.25 (s, 1 H, CH-4), 7.30−7.55 (m, 20 H, P−Ph). − $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 1.5 (s, CH_2−Si), 25.8 (t, $^2J_{CF}$ = 24 Hz, CH_2−CF_2), 36.2 (vt, CH_2−P), 100.0−126.0 (m, all C−F), 128.7 (d, $^3J_{CP}$ = 6.72 Hz, *m*-Ph), 129.2 (s, *p*-Ph), 131.1 (s, Si−C_{quat}), 132.4 (m, CH-4), 133.4 (d, $^2J_{CP}$ = 18 Hz, *o*-Ph), 138.2 (m, C_{quat}−CH_2PPh_2), 138.4 (d, $^1J_{CP}$ = 15 Hz, C_{quat} of P−Ph); CH-2,6 was not found. − $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ = −8.66 (s). − $^{29}Si\{^1H\}$ NMR (60 MHz, $CDCl_3$): δ = 0.49 (s).

Synthesis of [RuCl{4-Br-2,6-$(CH_2PPh_2)_2C_6H_2$}(PPh_3)] (6). − Method A: A solution of 1-Br-3,5-$(CH_2PPh_2)_2C_6H_3$ (0.58 g,

1.1 mmol) in 1,2-dichloroethane (10 mL) was added dropwise to a hot solution of $[RuCl_2(PPh_3)_3]$ (1.05 g, 1.1 mmol) in 40 mL of the same solvent. After refluxing for 2 h, the volatiles were removed under reduced pressure and the remaining solid was washed sequentially with hexane (2 × 5 mL), a 1:1 mixture of hexane/diethyl ether (1 × 5 mL), and diethyl ether (2 × 5 mL). Yield: 0.72 g (72%).

Method B: Complex **9** (0.0681 g, containing 11% of **10**) and $[RuCl_2(PPh_3)_3]$ (0.0316 g, 0.033 mmol) were dissolved in CH_2Cl_2 (10 mL) and the solution was refluxed overnight. The volatiles were then removed under reduced pressure and the remaining solid was washed sequentially with hexane (2 × 5 mL), a 1:1 mixture of hexane/diethyl ether (1 × 5 mL), and diethyl ether (2 × 5 mL). Yield: 0.0500 g (50%).

6: M.p. > 200 °C. − $C_{50}H_{41}BrClP_3Ru$ (951.2): calcd. C 63.13, H 4.34, P 9.77, Cl 3.73, Br 8.40, Ru 10.63; found C 63.08, H 4.26, P 9.65, Cl 3.79, Br 8.28, Ru 10.78. − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.37 (br. d, $^2J_{HH}$ = 16 Hz, 2 H, CH_2), 3.45 (dvt, $^2J_{HH}$ = 16 Hz, $^2J_{HP}$ = 6 Hz, 2 H, CH_2), 6.86 (m, 6 H, *m*-PPh_3), 6.95 (m, 4 H, *m*-PPh_2), 7.08 (m, 6 H, *o*-PPh_3), 7.11 (m, 4 H, *o*-PPh_2), 7.12−7.15 (m, 5 H, *p*-PPh_2 and *p*-PPh_3), 7.13 (2 H, CH-3,5), 7.39 (m, 4 H, *m*-PPh_2), 7.44 (m, 2 H, *p*-PPh_2), 7.85 (m, 4 H, *o*-PPh_2). − ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 39.1 (vt, $^{vt}J_{CP}$ = 15 Hz, CH_2), 116.0 (s, C−Br), 125.7 (vt, $^{vt}J_{CP}$ = 9 Hz, C-3,5), 127.4 (d, $^3J_{CP}$ = 10 Hz, *m*-PPh_3), 128.4 (vt, $^{vt}J_{CP}$ = 4 Hz, *m*-PPh_2), 128.8 (vt, $^{vt}J_{CP}$ = 4 Hz, *m*-PPh_2), 129.45−129.50 (two s, *p*-PPh_3 and *p*-PPh_2), 130.3 (s, *p*-PPh_2), 132.7 (vt, $^{vt}J_{CP}$ = 5 Hz, *o*-PPh_2), 133.1 (vt, $^{vt}J_{CP}$ = 5 Hz, *o*-PPh_2), 134.0 (m, C_{quat}−PPh_2), 134.4 (d, $^2J_{CP}$ = 10 Hz, *o*-PPh_3), 135.5 (vt, $^{vt}J_{CP}$ = 17 Hz, C_{quat}−PPh_2), 136.4 (d, $^1J_{CP}$ = 52 Hz, C_{quat}−PPh_3), 153.0 (vt, $^{vt}J_{CP}$ = 9 Hz, C-2,6), 172.8 (d, $^2J_{CP}$ = 17 Hz, Ru−C_{ipso}). − ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ = 36.74 (d, 2 P, Br−PCP), 80.62 (t, $^2J_{PP}$ = 32 Hz, 1 P, PPh_3).

Synthesis of [RuCl{$C_6H_2(CH_2PPh_2)_2$-2,6-Si(*n*-$CH_2CH_2C_8F_{17})_3$-4}-(PPh_3)] (7): $[RuCl_2(PPh_3)_3]$ (0.16 g, 0.17 mmol) and *meta*-bis(phosphane) **4** (0.31 g, 0.17 mmol) were dissolved in 1,2-dichlorobenzene and the solution was refluxed for 2 h. The volatiles were then removed under reduced pressure and the green-colored solid residue was extracted with FC-72 (5 × 2 mL). The insoluble material (free PPh_3) was separated from the green solution by filtration through Celite mounted in a disposable pipette. This extraction−filtration operation was performed twice in order to obtain the final product **7** free from PPh_3. Yield: 0.27 g (0.12 mmol, 71%). − FAB-MS showed a fragmentation peak at *m*/*z* = 2205.71 [M^+ − Cl] and also peaks characteristic of the loss of C_nF_m fragments. − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.90−1.10 (m, 6 H, CH_2−Si), 1.95−2.25 (m, 6 H, CF_2−CH_2), 2.73 (br. d, $^2J_{HH}$ = 16 Hz, 2 H, CH_2−P), 3.44 (m, 2 H, CH_2−P), 6.20−7.90 (m, aromatic), 8.08 (br. s, 4 H, *o*-PPh_2). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.5 (s, CH_2−Si), 26.0 (t, $^3J_{CF}$ = 24 Hz, *C*H_2−CF_2), 38.9 (t, $^1J_{CP}$ = 15 Hz, CH_2−P), 100.0−124.0 (m, CF_n), 121.8 (s), 127.1 (d, $^4J_{CP}$ = 11 Hz, *m*-PPh_3), 128.06 (vt, *m*-PPh_2), 128.59 (m, *m*-PPh_2), 129.0−129.5 (m, *p*-PPh_3 and *p*-PPh_2), 130.1 (s, *p*-PPh_2), 132.5 (vt, *o*-PPh_2), 134.1 (d, $^3J_{CP}$ = 8 Hz, *o*-PPh_3), 135.6 (m, C_{quat}), 136.7 (s, C_{quat}), 151.9 (vt, C_{quat}); resonances of Ru−C_{ipso} and C_{quat}−PPh_2 were too weak to be located). − ^{31}P{^{1}H} NMR (81 MHz, C_6D_6): δ = 36.11 (d, 2 P, PPh_2), 82.26 (t, $^2J_{PP}$ = 32 Hz, 1 P, PPh_3).

Synthesis of [{RuCl[$C_6H_2(CH_2PPh_2)_2$-2,6-Br-4]}$_2${μ-η^1-*P*,η^1-*P*′-[$C_6H_3(CH_2PPh_2)_2$-3′,5′-Br-1′]}] (9) and (10). − Method A: A solution of $[RuCl_2(PPh_3)_3]$ (0.96 g, 1.0 mmol) and **3** (1.11 g, 2.0 mmol) in CH_2Cl_2 (30 mL) was refluxed for 3 days. The volatiles were then removed under reduced pressure and the residual dark-green material was washed with hexane (8 × 10 mL) and Et_2O (2 × 4 mL). After drying in vacuo, 0.95 g of a light-green solid was obtained, which was found to consist of **9** (89%) and **10** (11%).

Method B: Addition of ligand **3** (0.0200 g, 0.0360 mmol) to a solution of **6** (0.0688 g, 0.0720 mmol) in CH_2Cl_2 (10 mL) and stirring for 1 h at room temp. led to a mixture of complexes **9** and **10** in a 2:1 ratio. However, starting materials were still present, despite the use of excess ligand, which thwarted the isolation of **9** and **10** from the reactants after the standard work-up (see above) with hexane and Et_2O.

[{RuCl[$C_6H_2(CH_2PPh_2)_2$-2,6-Br-4]}$_2${μ-η^1-*P*,η^1-*P*′-[$C_6H_3(CH_2PPh_2)_2$-3′,5′-Br-1′]}] (9): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (br. d, $^2J_{HH}$ = 16 Hz, 4 H, CH_2 of Br−PCP), 3.10 (d, $^2J_{HP}$ = 9 Hz, 4 H, CH_2 of Br−PCHP), 3.63 (dm, $^2J_{HH}$ = 16 Hz, 4 H, CH_2 of Br−PCP), 4.82 (s, 1 H, CH-4′), 5.47 (s, 2 H, CH-2′,3′), 6.30−7.90 (m, aromatic), 8.00−8.20 (m, 8 H, *o*-PPh_2). − ^{13}C{^{1}H} NMR (75.5 MHz, CD_3Cl): δ = 39.6 (m, all CH_2), 115.3 (s, C−Br of Br−PCP), 119.9 (s, C−Br of Br−PCHP), 125.0 (m, aromatic CH), 126.8 (m, aromatic CH), 128.3 (m, aromatic CH), 128.6 (m, aromatic CH), 129.1 (s, aromatic CH), 129.8 (s, aromatic CH), 130.3 (m, aromatic CH), 131.1 (m), 131.7 (m, aromatic CH), 132.8 (d, J_{CP} = 9 Hz, aromatic CH), 133.0 (m), 134.2 (m, C_{quat}), 136.2 (d, J_{CP} = 12 Hz, C_{quat}), 151.3 (vt, $^{vt}J_{CP}$ = 9 Hz, C-2,6 of Br−PCP), 173.9 (br. d, $^2J_{CP}$ = 16 Hz, Ru−C_{ipso}). − ^{31}P{^{1}H} NMR (81 MHz, CD_3Cl): δ = 40.05 (d, 4 P, Br−PCP), 83.75 (t, $^2J_{PP}$ = 31 Hz, 2 P, Br−PCHP).

[RuCl{$C_6H_2(CH_2PPh_2)_2$-2,6-Br-4}{η^1-*P*-[$C_6H_3(CH_2PPh_2)_2$-3′,5′-Br-1′]}] (10): Due to the low concentration of this compound, as well as to overlap with the stronger signals of the bridging complex, only a few of its ^{1}H NMR resonances could be assigned. For the same reasons, the carbon resonances were to weak too be detected. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (m, 2 H, CH_2 of the non-coordinated CH_2PPh_2 group), 3.30−3.80 (m, 6 H, CH_2 of the coordinated CH_2PPh_2 groups), 5.68 (s, 1 H, CH-2′ or 4′ or 6′), 5.82 (s, 1 H, CH-2′ or 4′ or 6′), 5.90 (s, 1 H, CH-2′ or 4′ or 6′). − ^{31}P{^{1}H} NMR (81 MHz, CD_3Cl): δ = −10.06 (s, 1 P, non-coordinated PPh_2), 40.3 (d, 2 P, Br−PCP), 83.8 (t, 1 P, coordinated PPh_2 of Br−PCHP , $^2J_{PP}$ = 31 Hz).

Synthesis of [{RuCl[$C_6H_3(CH_2PPh_2)_2$-2,6]}$_2${μ-η^1-*P*,η^1-*P*′-[C_6H_4-$(CH_2PPh_2)_2$-1′,3′]}] (11): A solution of $RuCl_3{\cdot}3H_2O$ (0.18 g, 0.70 mmol) in methanol (10 mL) was refluxed for 1 h. Compound **5** (0.50 g, 1.05 mmol) was then added as a solid and reflux was continued overnight. After removal of the volatiles under reduced pressure, pure **11** could be extracted from the green-colored solid residue with benzene. Yield: 0.0700 g (14%). − ^{1}H NMR (300 MHz, C_6D_6): δ = 2.81 (br. d, $^2J_{HH}$ = 16 Hz, 4 H, CH_2 of H−PCP), 3.42 (d, $^2J_{HP}$ = 9 Hz, 4 H, CH_2 of H−PCHP), 3.62 (dvt, $^2J_{HH}$ = 16 Hz, 4 H, CH_2 of H−PCP), 5.42 (s, 1 H, CH-2′), 5.69 (d, $^3J_{HH}$ = 8 Hz, 2 H, CH-2′,4′), 5.99 (t, $^3J_{HH}$ = 8 Hz, 1 H, CH-3′), 6.60−6.85 (m, 22 H, aromatic), 6.90−7.25 (m, 26 H, aromatic), 7.35−7.45 (m, 10 H, aromatic), 8.10−8.20 (m, 8 H, *o*-Ph); not all resonances were detected due to overlapping with C_6D_6 carbon signal. − ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 40.6 (m, all CH_2), 121.6 (s, CH aromatic), 122.9 (t, J_{CP} = 9 Hz), 126.6 (s), 126.9 (d, J_{CP} = 10 Hz), 130.8−131.3 (m), 132.4 (vt, $^{vt}J_{CP}$ = 5 Hz), 133.5−133.9 (m), 135.2−136.1 (m), 151.1 (vt, $^{vt}J_{CP}$ = 9 Hz, C_{quat}, C-2,6), 175.3−175.9 (m, Ru−C_{ipso}). − ^{31}P{^{1}H} NMR (81 MHz, C_6D_6): δ = 40.90 (d, 4 P, H−PCP), 85.22 (t, $^2J_{PP}$ = 32 Hz, 2 P, H−PCHP).

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